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Polarization dependence of X-ray emission spectroscopy

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Abstract

The polarization dependence of X-ray emission spectroscopy (XES) is studied on the angle dependence of incident and emitted X-ray. The Kramers–Heisenberg formula is employed to describe the optical process. It is shown that the quantum mechanical interference effect is directly observable in magnetic circular dichroism (MCD) spectra in a special geometrical configuration. It is also shown that by making use of the linearly polarized X-ray, information on the symmetry of ground states of materials is directly determinable from simple selection rules. Potential possibilities of X-ray spectrum with a polarized photon are demonstrated.

Keywords: Polarized X-ray; X-ray emission spectroscopy; Magnetic circular dichroism

1. Introduction

The study of X-ray emission spectroscopy (XES) has made remarkable progress in recent years with the use of high-brilliance synchrotron radiation sources [1]. There is a great advantage in the X-ray from synchrotron radiation sources, because of its polarized nature. There has been a great progress in the study of X-ray spectroscopy, especially in X-ray absorption spectroscopy (XAS), using linearly and circularly polarized X-rays in the last decades [2,3]. It is expected that there is potential possibilities in the study of XES with polarized X-ray.

In the interpretation of XES, the Kramers–Heisenberg formula [4], which describes a coherent second-order optical process, have been widely used. A quantum mechanical interference effect is taken into account in this formula. There has been almost no direct justification for the usage of this formulation for XES to the authors' knowledge. It is interesting to evaluate the contribution from the interference effect separately.

Recent experiments observed a non-vanishing magnetic circular dichroism (MCD) signal with a geometry of the direction of the incident X-ray is perpendicular to the magnetic moment [5–7], where no MCD signal is expected for XAS. It is a bit surprising because the polarization of the emitted X-ray is not resolved. This implies a need for a model beyond a combination of two successive independent first order optical process [8].

In this paper the polarization dependence of XES is studied from the view point of geometrical symmetry. We show that the MCD of XES in the above case originates from interference term of coherent second-order process. We also investigate the case where the incident X-ray is linearly polarized.

In the next section a formulation required for the calculation of XES are presented. In Section 3, results for XES with polarized X-ray are given and discussed. A different theoretical approach is also presented to clarify the angle dependence of MCD. In the final section we give concluding remarks.

2. Formulation

2.1. Wave vector

We assume a photon as a plane wave of wave vector $\vec{k}$ and polarization vector $\vec{e}$. It is convenient to use a photon energy $\omega = c|\vec{k}|$ and a polar angle (θ, ϕ) of the direction of

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propagation to specify a photon. Here c is the velocity of light. The direction of $\vec{k}$ is given, in the Cartesian coordinate, as

$$\frac{\vec{k}}{|\vec{k}|} = (\sin\theta\cos\varphi,\ \sin\theta\sin\varphi,\ \cos\theta), \tag{1}$$

which is in the tensor form,

$$\begin{cases} k^{(1)}_1 = -\dfrac{1}{\sqrt{2}}\sin\theta e^{i\varphi} \\ k^{(1)}_0 = \cos\theta \\ k^{(1)}_{-1} = \dfrac{1}{\sqrt{2}}\sin\theta e^{-i\varphi} \end{cases} \tag{2}$$

from the definition of tensor of rank 1,

$$\begin{cases} w^{(1)}_1 \equiv -\dfrac{1}{\sqrt{2}}(w_x + iw_y) \\ w^{(1)}_0 \equiv w_z \\ w^{(1)}_{-1} \equiv \dfrac{1}{\sqrt{2}}(w_x - iw_y). \end{cases} \tag{3}$$

2.2. Polarization vector

The polarization vector $\vec{e}$ is perpendicular to the wave vector $\vec{k}$, i.e. $\vec{e} \perp \vec{k}$. Thus there remain two independent directions in the polarization direction of a photon.

We define a Cartesian coordinate system at the point of $\vec{k}$ with unit vectors of,

$$\begin{cases} \hat{k}_r = \sin\theta\cos\varphi\hat{x} + \sin\theta\sin\varphi\hat{y} + \cos\theta\hat{z} \\ \hat{k}_\theta = \cos\theta\cos\varphi\hat{x} + \cos\theta\sin\varphi\hat{y} - \sin\theta\hat{z} \\ \hat{k}_\varphi = -\sin\varphi\hat{x} + \cos\varphi\hat{y}. \end{cases} \tag{4}$$

Here $\hat{k}_r$ is in the direction of $\vec{k}$.

A circularly polarized photon is designated by helicity $\lambda = \pm 1$. The polarization vector of a circularly polarized photon is given in this coordinate as

$$\vec{e}(\lambda = \pm 1) = \mp\frac{1}{\sqrt{2}}(0, 1, \pm i). \tag{5}$$

A linearly polarized photon is designated by polarization angle θ^{p}. If we define that the polarization angle is measured from the direction of $\hat{k}_\theta$, the polarization vector is given as,

$$\vec{e}(\theta^{p}) = (0,\ \cos\theta^{p},\ \sin\theta^{p}). \tag{6}$$

Thus the tensor form of these polarization vectors in the original coordinate are given as,

$$\begin{cases} e^{(1)}_1 = -\frac{1}{2}(1 \mp \cos\theta)e^{i\varphi} \\ e^{(1)}_0 = \pm\dfrac{1}{\sqrt{2}}\sin\theta \\ e^{(1)}_{-1} = -\frac{1}{2}(1 \pm \cos\theta)e^{-i\varphi} \end{cases} \tag{7}$$

for the circularly polarized photon of helicity $\lambda = \pm 1$ and

$$\begin{cases} e^{(1)}_1 = -\dfrac{1}{\sqrt{2}}(\cos\theta^{p}\cos\theta + i\sin\theta^{p})e^{i\varphi} \\ e^{(1)}_0 = -\cos\theta^{p}\sin\theta \\ e^{(1)}_{-1} = \dfrac{1}{\sqrt{2}}(\cos\theta^{p}\cos\theta - i\sin\theta^{p})e^{-i\varphi} \end{cases} \tag{8}$$

for the linearly polarized photon of polarization angle θ^{p}.

2.3. Transition operator

The perturbation treatment is appropriate for the description of the interaction between electronic system and the X-ray from synchrotron radiation sources. The perturbation operator for photo absorption transition is expressed in the non-relativistic limit,

$$T \propto \vec{e}\cdot\vec{r}e^{i\vec{k}\cdot\vec{r}} \sim \vec{e}\cdot\vec{r}(1 + i\vec{k}\cdot\vec{r} + \cdots). \tag{9}$$

This expansion is valid in the long wavelength limit. In this expansion, the first term gives dipole transition operator and the second term quadrupole transition operator.

We define the dipole transition operator for photon absorbing process as

$$T^{(1)}_a \equiv \vec{e}\cdot\vec{r} \tag{10}$$

$$= r\sum_{q=-1}^{1}(-)^q e^{(1)}_{-q}C^{(1)}_q. \tag{11}$$

The dipole transition operator for photon emitting process is given as Hermite conjugate of $T^{(1)}_a$.

$$T^{(1)}_e \equiv (T^{(1)}_a)^\dagger \tag{12}$$

$$= r\sum_{q=-1}^{1}(-)^q \bar{e}^{(1)}_{-q}C^{(1)}_q, \tag{13}$$

where $\bar{e}$ is defined as,

$$\bar{e}^{(1)}_q \equiv (-)^q e^{(1)*}_{-q}. \tag{14}$$

The superscript symbols $\dagger$ and $*$ represent Hermite and complex conjugate, respectively.

The quadrupole transition operator for absorption process is defined as,

$$T^{(2)}_a \equiv (\vec{e}\cdot\vec{r})(\vec{k}\cdot\vec{r}) \tag{15}$$

$$= r^2\sum_{q=-2}^{2}(-)^q\sqrt{\frac{2}{3}}[ek]^{(2)}_{-q}C^{(2)}_q, \tag{16}$$

the transformation from the first to the second line is given in the Appendix A. The symbol $[vw]^{(k)}_q$ represents tensor product and is defined as,

$$[vw]^{(k)}_q \equiv \sum_{q_1+q_2=q} v^{(k_1)}_{q_1}w^{(k_2)}_{q_2}\langle k_1k_2q_1q_2|kq\rangle, \tag{17}$$

where $\langle k_1k_2q_1q_2|kq\rangle$ is a Clebsch-Gordan symbol. The quadrupole transition operator for emission process is also given as the Hermite conjugate of the absorption operator.

2.4. Spectral function

We adopt a quantum mechanically coherent second-order optical model, i.e. Kramers–Heisenberg formula, to describe the X-ray emission spectroscopy. The spectral function of XES is given as

$$F(\omega_2,\omega_1)=\sum_f\left|\sum_i\frac{\langle f|T_2|i\rangle\langle i|T_1|g\rangle}{E_i-E_g-\hbar\omega_1-i\Gamma_i}\right|^2 \times\delta(E_f-E_g+\hbar\omega_2-\hbar\omega_1), \quad (18)$$

where $|g\rangle$, $|i\rangle$ and $|f\rangle$ are the ground, intermediate and final states with energies E_g, E_m and E_f, respectively, Γ_i represents the finite life time effect of the intermediate state, ω specifies photon energies, and the subscripts 1 and 2 discriminate incident and emitted process, respectively. The parameters to specify photon besides the photon energy (θ, φ and λ or θ^{p}) is implicitly included in T.

In the case of XES, T_1 is an absorption operator and T_2 is an emission operator. Because this formula is general expression for a coherent second-order optical process, it is applicable to other two-photon processes such as a two-photon absorption (T_1 and T_2 are both absorption operators) or a two-photon emission process (T_1 and T_2 are both emission operators).

2.5. Magnetic circular dichroism

The magnetic circular dichroism is defined as a difference between two spectrums for different photon helicities. We define MCD for XES (ΔF) as a difference between two spectrum of two different incident photons with helicity $\lambda=-1$ and $\lambda=+1$. Here we sum up on the helicities of the emitted photon. The MCD of XES is then written as

$$\Delta F\equiv(F^{+1-1}+F^{-1-1})-(F^{+1+1}+F^{-1+1}), \quad (19)$$

where the helicity of photons are written down explicitly as $F^{\lambda_2\lambda_1}$. The indices λ_1 and λ_2 specify the helicities for the incident and the emitted photon, respectively.

From the theoretical point of view, there is no inevitable reason to sum up on the emitted photon. It is possible to define MCD either on λ_1 or λ_2.

2.6. Two geometrical configurations for the linearly polarized X-ray

When considering a linearly polarized X-rays in XES, there are two special geometrical configurations, known as polarized geometry and depolarized geometry. Polarized configuration is defined as geometry where the polarization vector of the incident X-ray is perpendicular to the scattering plane. Depolarized configuration is defined as geometry where the polarization vector of the incident X-ray lies within the scattering plane. Here a scattering plane is defined as a plane spanned by the wave vectors of the incident photon $\vec{k}_1$ and the emitted photon $\vec{k}_2$.

3. Results

3.1. MCD of XES

In this subsection we discuss the MCD of XES of the dipole transitions in spherical symmetry under the condition that the magnetic moment lies in the z-direction (the quantization axis). In this case the spectral function is written as

$$F(\omega_2,\omega_1)=\sum_f\sum_{\Delta Q}\left|\sum_{q_1+q_2=\Delta Q}(-)^{q_1+q_2}e^{(1)}_{-q_2}e^{(1)}_{-q_1}f^{(1,1)}_{q_2,q_1}\right|^2 \times\delta(E_f-E_g+\hbar\omega_2-\hbar\omega_1), \quad (20)$$

where the symbol $f^{(l_2,l_1)}_{q_2,q_1}$ is defined as

$$f^{(l_2,l_1)}_{q_2,q_1}\equiv\sum_i\frac{\langle f|C^{(l_2)}_{q_2}|i\rangle\langle i|C^{(l_1)}_{q_1}|g\rangle}{E_f-E_g-\hbar\omega_1-i\Gamma_i}. \quad (21)$$

The subscript index 1 and 2 designate the absorbing and the emitting process, respectively.

Under the spherical symmetry the quantum mechanical interference may occur within the states of the same ΔQ. The terms for each ΔQ are

$$\begin{cases}\bar{e}^{(1)}_{-1}e^{(1)}_{-1}f^{(1,1)}_{1,1}, & (\Delta Q=2)\\ -\bar{e}^{(1)}_{-1}e^{(1)}_{0}f^{(1,1)}_{1,0}-\bar{e}^{(1)}_{0}e^{(1)}_{-1}f^{(1,1)}_{0,1}, & (\Delta Q=1)\\ \bar{e}^{(1)}_{-1}e^{(1)}_{1}f^{(1,1)}_{1,-1}+\bar{e}^{(1)}_{0}e^{(1)}_{0}f^{(1,1)}_{0,0} & \\ \quad+\bar{e}^{(1)}_{1}e^{(1)}_{0}f^{(1,1)}_{-1,1}, & (\Delta Q=0)\\ -\bar{e}^{(1)}_{1}e^{(1)}_{0}f^{(1,1)}_{-1,0}-\bar{e}^{(1)}_{0}e^{(1)}_{1}f^{(1,1)}_{0,-1}, & (\Delta Q=-1)\\ \bar{e}^{(1)}_{1}e^{(1)}_{1}f^{(1,1)}_{-1,-1}, & (\Delta Q=-2).\end{cases} \quad (22)$$

Inserting the explicit expressions into the polarization vectors $\bar{e}$ and e after Eq. (7) and making addition and subtraction after the definition Eq. (19), we obtain a formula for MCD as

$$\begin{aligned}\Delta F=&-\cos\theta_1\left\{\tfrac{1}{2}(1+\cos^2\theta_2)(|f_{11}|^2+|f_{-11}|^2\right.\\&\left.-|f_{1-1}|^2-|f_{-1-1}|^2)+\sin^2\theta_2(|f_{01}|^2-|f_{0-1}|^2)\right\}\\&-\tfrac{1}{4}\sin\theta_1\{\sin2\theta_2(f^*_{10}f_{01}+f^*_{01}f_{10}+f^*_{1-1}f_{00}\\&+f^*_{00}f_{1-1}-f^*_{-10}f_{0-1}-f^*_{0-1}f_{-10}\\&-f^*_{-11}f_{00}-f^*_{00}f_{-11})\},\end{aligned} \quad (23)$$

where the symbol $f_{q_2q_1}$ is defined as

$$f_{q_2q_1}\equiv\mathrm{e}^{-\mathrm{i}q_2\varphi_2}\mathrm{e}^{-\mathrm{i}q_1\varphi_1}f^{(1,1)}_{q_2,q_1}. \quad (24)$$

The first term proportional to $\cos\theta_1$ originates only from the diagonal term and has the same incident angle dependence as the XAS. The second term proportional to $\sin\theta_1$ originates only from the off-diagonal interference term. The first term meets with the intuitive two-step model and we can guess the $\cos\theta_1$ dependence originates from the exciting step, while the second term is unexpected from intuitive model and purely a quantum mechanical effect.

If the incident photon is parallel to the magnetic moment ($\theta_1 = 0$), the interference term vanishes, while if it is perpendicular to the magnetic moment ($\theta_1 = \pi/2$), only the interference term remains. The non-vanishing MCD are observed experimentally and the angle dependence both for the θ_1 and θ_2 are also reproduced fairly well. This is a direct justification of the use of the Kramers–Heisenberg formula for XES.

3.2. Fundamental spectrum

In the expression above on the MCD of XES (ΔF), the angle dependence suggest the some symmetry relation behind it. The dependence on the incident angle θ_1 corresponds to the p symmetry, while the dependence on the emitting angle θ_2 suggest the d symmetry.

In this subsection we derive the expression for MCD again with different view point by means of fundamental spectrum proposed by Thole and van der Laan [9]. We define a new tensor operator $I_q^{l(k)}$ as

$$I_q^{l(k)} \equiv \sum_{q_1,q_2} (-)^{1-q_1} \begin{pmatrix} l & k & l \\ -q_1 & q & q_2 \end{pmatrix} C_{q_1}^{(l)*} C_{q_2}^{(l)} \times \begin{pmatrix} l & k & l \\ -l & 0 & l \end{pmatrix}^{-1}, \tag{25}$$

where the bracket represents $3j$-symbol and $C_q^{(l)}$ renormalized spherical tensor.

We start from the special case where the incident and the emitted photon are parallel to the z-axis. In this geometry, the MCD operator is written as

$$(C_{-1}^{(1)})^* C_{-1}^{(1)} - (C_{+1}^{(1)})^* C_{+1}^{(1)} = -I_0^{1(1)}, \tag{26}$$

where the normalized spherical tensors are supposed to be applied on the appropriate states. The sum over the polarization of the emitting photon is written as

$$(C_{-1}^{(1)})^* C_{-1}^{(1)} + (C_{+1}^{(1)})^* C_{+1}^{(1)} = \tfrac{1}{3}(2I_0^{1(0)} + I_0^{1(2)}). \tag{27}$$

The operator for MCD of XES in this special geometry is written with these relations as

$$\Delta F = -\tfrac{1}{3}(2I_0^{1(0)} + I_0^{1(2)}) I_0^{1(1)}. \tag{28}$$

By making use of a property of the spherical harmonics

$$I_0^{l(k)} = \sum_q (-1)^q C_q^{(k)} I_q^{l(k)}, \tag{29}$$

the operator for the general direction is derived as

$$\Delta F = -\tfrac{1}{3}(2C_0^{(0)} I_0^{1(0)} + C_0^{(2)} I_0^{1(2)}) C_0^{(1)} I_0^{1(1)} - \tfrac{1}{3}(C_{-1}^{(2)} I_{-1}^{1(2)} C_{+1}^{(1)} I_{+1}^{1(1)} + C_{+1}^{(2)} I_{+1}^{1(2)} C_{-1}^{(1)} I_{-1}^{1(1)}). \tag{30}$$

Inserting explicit expressions in this formula, we obtain

$$\begin{aligned}\Delta F = &-\cos\theta_1 \Big\{ \tfrac{1}{2}(1+\cos^2\theta_2)(c_1^* c_1 + c_{-1}^* c_{-1}) \\ &\times (c_1^* c_1 - c_{-1}^* c_{-1}) + \sin^2\theta_2 c_0^* c_0 (c_1^* c_1 - c_{-1}^* c_{-1}) \Big\} \\ &+ \tfrac{1}{4}\sin\theta_1 \sin 2\theta_2 \{ e^{-i(\varphi_2-\varphi_1)} (c_0^* c_1 - c_{-1}^* c_0) \\ &\times (c_0^* c_{-1} + c_1^* c_0) - e^{i(\varphi_2-\varphi_1)} (c_0^* c_{-1} - c_1^* c_0) \\ &\times (c_0^* c_1 + c_{-1}^* c_0) \},\end{aligned} \tag{31}$$

where c_q is an abbreviation of $C_q^{(1)}$.

When this operator is applied to appropriate states, we reproduce the result in the previous subsection as

$$\begin{aligned}\Delta F = &-\cos\theta_1 \Big\{ \tfrac{1}{2}(1+\cos^2\theta_2)(|f_{11}|^2 + |f_{-11}|^2 - |f_{1-1}|^2 \\ &- |f_{-1-1}|^2) + \sin^2\theta_2 (|f_{01}|^2 - |f_{0-1}|^2) \Big\} \\ &- \tfrac{1}{4}\sin\theta_1 \sin 2\theta_2 \{ e^{-i(\varphi_2-\varphi_1)} (f_{00}^* f_{1-1} + f_{01}^* f_{10} \\ &- f_{-10}^* f_{0-1} - f_{-11}^* f_{00}) - e^{i(\varphi_2-\varphi_1)} (f_{00}^* f_{-11} \\ &+ f_{0-1}^* f_{-10} - f_{10}^* f_{01} - f_{1-1}^* f_{00}) \}.\end{aligned} \tag{32}$$

From these expressions the origin of the symmetry of the angle dependence is clearly understood. The p-symmetry of the incident angle θ_1 is the direct consequence of the MCD operator $I_q^{1(1)}$. The angle dependence on the emitted photon θ_2 is a linear combination of the s and d symmetry for the diagonal term while the angle dependence is only from the term $I_{\pm 2}^{11(2)}$ and thus have pure d-symmetry for the interference term.

3.3. MCD of quadrupole excitation

We apply the method in the previous subsection to the quadrupole excitation. Here it is assumed that the excitation is expressed by quadrupole transition operator, while the emitting process remains the same dipole transition.

The MCD operator for the quadrupole transition is derived as

$$(C_{-1}^{(2)})^* C_{-1}^{(2)} - (C_{+1}^{(2)})^* C_{+1}^{(2)} = -\tfrac{2}{5}(I_0^{2(1)} - I_0^{2(3)}). \tag{33}$$

The MCD operator for the z-direction is written as

$$\Delta F = -\tfrac{2}{15}(2I_0^{1(0)} + I_0^{1(2)})(I_0^{2(1)} - I_0^{2(3)}). \tag{34}$$

The operator for arbitrary direction is

$$\begin{aligned}\Delta F = &-\tfrac{2}{15}(2C_0^{(0)} I^{1(0)} + C_0^{1(2)} I_0^{(2)})(C_0^{(1)} I_0^{2(1)} - C_0^{(3)} I_0^{2(3)}) \\ &- \tfrac{2}{15}(C_{-1}^{(2)} I_{-1}^{1(2)} (C_1^{(1)} I_1^{2(1)} - C_1^{(3)} I_1^{2(3)}) \\ &+ C_1^{(2)} I_1^{1(2)} (C_{-1}^{(1)} I_{-1}^{2(1)} - C_{-1}^{(3)} I_{-1}^{2(3)})) \\ &+ \tfrac{2}{15}(C_{-2}^{(2)} I_{-2}^{1(2)} C_2^{(3)} I_2^{2(3)} + C_2^{(2)} I_2^{1(2)} C_{-2}^{(3)} I_{-2}^{2(3)}).\end{aligned} \tag{35}$$

Inserting explicit expressions in this formula, we obtain

$$\begin{aligned}\Delta F = {} & \tfrac{1}{2}[\sin^2\theta_1\{(1+\cos^2\theta_2)(|f_{1-2}|^2+|f_{-1-2}|^2 \\ & -|f_{-12}|^2-|f_{-12}|^2)+2\sin^2\theta_2(|f_{0-2}|^2-|f_{02}|^2)\} \\ & +\cos 2\theta_1\{(1+\cos^2\theta_2)(|f_{1-1}|^2+|f_{-1-1}|^2 \\ & -|f_{11}|^2-|f_{-11}|^2)+2\sin^2\theta_2(|f_{0-1}|^2-|f_{01}|^2)\}] \\ & +\frac{1}{4}\sin\theta_1\Big[\sqrt{3}\cos^2\theta_1\sin 2\theta_2\{e^{-i(\varphi_2-\varphi_1)}(f^*_{01}f_{10} \\ & +f^*_{00}f_{1-1}-f^*_{-10}f_{0-1}-f^*_{-11}f_{00})+e^{i(\varphi_2-\varphi_1)} \\ & \times(f^*_{10}f_{01}+f^*_{1-1}f_{00}-f^*_{0-1}f_{-10}-f^*_{00}f_{-11})\} \\ & -\sqrt{\tfrac{1}{2}}(\cos^2\theta_1+\cos 2\theta_1)\sin 2\theta_2\times\{e^{-i(\varphi_2-\varphi_1)} \\ & \times(f^*_{02}f_{11}+f^*_{0-1}f_{1-2}-f^*_{-12}f_{01}-f^*_{-1-1}f_{0-2}) \\ & +e^{i(\varphi_2-\varphi_1)}(f^*_{11}f_{02}+f^*_{1-2}f_{0-1}-f^*_{01}f_{-12} \\ & -f^*_{0-2}f_{-1-1})\}-\sqrt{\tfrac{3}{2}}\sin 2\theta_1\sin^2\theta_2\{e^{-2i(\varphi_2-\varphi_1)} \\ & \times(f^*_{-12}f_{10}-f^*_{-10}f_{1-2})+e^{2i(\varphi_2-\varphi_1)} \\ & \times(f^*_{10}f_{-12}-f^*_{1-2}f_{-10})\}\Big].\end{aligned} \tag{36}$$

This reproduces the result by Fukui et al. [7]. The angle dependence is different for each ΔQ and the origin of the symmetrical properties of the angle dependence is clear.

3.4. Depolarized configuration

In this subsection we discuss a special characteristic of the depolarized configuration for the linearly polarized X-ray [13]. We restrict ourselves to the case where the z-axis, which is assumed as the direction of quantization, is in the scattering plane. The polarization angle θ^{p} of the polarized configuration is $\pi/2$ and that of the depolarized configuration is 0. The polarization vector is written as

$$\begin{cases} e_1^{(1)} = -\dfrac{1}{\sqrt{2}}\cos\theta\mathrm{e}^{\mathrm{i}\varphi} \\ e_0^{(1)} = -\sin\theta \\ e_{-1}^{(1)} = \dfrac{1}{\sqrt{2}}\cos\theta\mathrm{e}^{-\mathrm{i}\varphi}. \end{cases} \tag{37}$$

When this polarization vector is multiplied by a polarization vector of emitted photon with an arbitrarily polarization angle, the term with the total magnetic momentum change of zero ($q_1+q_2=0$) becomes

$$\bar{e}^{(1)}_{-1}e^{(1)}_1+\bar{e}^{(1)}_0e^{(0)}_1+\bar{e}^{(1)}_{-1}e^{(1)}_1=-\cos\theta^{\mathrm{p}}_2\cos(\theta_2-\theta_1). \tag{38}$$

It is easily seen that this term will vanish regardless of the polarization angle θ_2^p if the scattering angle $|\theta_2-\theta_1|$ is equal to $\pi/2$.

From this finding it is concluded that with the depolarized configuration the initial state $|g\rangle$ and the final state $|f\rangle$ cannot have an identical magnetic quantum number under spherical symmetry. This implies that the elastic scattering is forbidden when the initial state is non-degenerate as in the case of $|J=0, M=0\rangle$.

This characteristic of depolarized geometry is also applicable to lower symmetrical systems in somewhat restricted form. In the case of octahedral symmetry, it is deduced that if the elastic line vanishes for the depolarized configuration the initial state is either A_1 or A_2 [10–12].

4. Concluding remarks

In the present paper we gave a general expression for the MCD of RXES for arbitrary directions of incident and emitted X-ray photons from geometrical arguments. It was shown that the non-vanishing MCD originates from the quantum mechanical interference effect, when the incident photon is perpendicular to the magnetic moment. The result was also derived using the idea of fundamental spectrum. The angle dependence of MCD was directly obtained from the symmetry of spherical tensors. The angle dependence of the incident and the emitted photons in the present theory is observed in the experiment [6,7].

It is also shown that with the linearly polarized incident X-ray in the depolarized configuration, the elastic scattering is forbidden when the ground state is not degenerate from the symmetry selection rule. Using the selection rule of XES with linearly polarized X-ray, it is possible to determine the symmetry of the ground state and the excited states nearby from the angle dependence of XES. This relations have been explored on the 4f rare-earth and 5f actinides systems [13] and 3d transition metal systems as well [10–12, 14].

These facts directly justify the use of the Kramers–Heisenberg formula to describe the X-ray emission spectroscopy. The present result is general and applicable to similar second-order optical processes such as two-photon absorption and two-photon emission [15]. In the present paper some of the potential possibilities of X-ray spectroscopy using polarized X-ray are demonstrated.

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Appendix A

The quadrupole transition operator can be expressed in the tensor form as,

$$(\vec{e}\cdot\vec{r})(\vec{k}\cdot\vec{r})=3[[er]^{(0)}[kr]^{(0)}]^{(0)}_0. \tag{A.1}$$

By recoupling the vectors,

$$[[er]^{(0)}[kr]^{(0)}]^{(0)}_0 = \sum_K (2K+1) \begin{Bmatrix} 1 & 1 & 0 \\ 1 & 1 & 0 \\ K & K & 0 \end{Bmatrix} \times [[ek]^{(K)}[rr]^{(K)}]^{(0)}_0 \tag{A.2}$$

$$= \sum_K \frac{\sqrt{2K+1}}{3} [[ek]^{(K)}[rr]^{(K)}]^{(0)}_0. \tag{A.3}$$

The terms for $K = 0$ and $K = 1$ vanish by the conditions $\vec{e} \cdot \vec{k} = 0$ and $\vec{r} \times \vec{r} = 0$, respectively. Using the property of spherical tensor,

$$[C^{(k_1)}_{q_1} C^{(k_2)}_{q_2}]^{(K)}_Q = (-)^K \sqrt{2K+1} \begin{Bmatrix} k_1 & k_2 & K \\ 0 & 0 & 0 \end{Bmatrix} C^{(K)}_Q, \tag{A.4}$$

the expression $[rr]^{(2)}_q$ is reduced to

$$[rr]^{(2)}_q = \sqrt{\frac{2}{3}} r^2 C^{(2)}_q. \tag{A.5}$$

Hence the quadrupole operator is

$$(\vec{e} \cdot \vec{r})(\vec{k} \cdot \vec{r}) = \sqrt{5}[[ek]^{(2)} \sqrt{\frac{2}{3}} r^2 C^{(2)}]^{(0)}_0 \tag{A.6}$$

$$= r^2 \sum_q (-)^q \sqrt{\frac{2}{3}} [ek]^{(2)}_{-q} C^2_q. \tag{A.7}$$

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